**REMARKS** 

A Final Rejection was mailed in the present case on October 21, 2009, making a response due on

or before January 21, 2010. This Response accompanies a Request For Continued Examination and

the required fee for the RCE. No additional fee is thought to be due at this time. If any additional fee

is due for the continued prosecution of this application, please charge the same to Applicant's

Deposit Account No. 50-2555 (Whitaker, Chalk, Swindle & Sawyer, LLP).

Applicant's pending Claims 1-6 presently stand rejected under 35 U.S.C. §103(a) as being

unpatentable over Huege et al. (US 5616283). In the previous response filed in the case, Applicant

argued that the specific surface area disclosed by Huege et al., which broadly encompasses the

claimed range, only refers to external specific surface area, while the BET specific surface area

recited in the instant application includes internal specific surface area. In support of this position,

Applicant submitted the Declaration of Professor Jean-Paul Pirard, an expert on specific surface area

and porosity measurements. However, the Examiner has countered Applicant's argument on the basis

that no evidence has been submitted showing that the solid matter in the Huege et al. reference is,

in fact, porous. The Examiner argues that, with the solid matter in Huege et al. being non-porous,

or with negligible porosity, the specific surface area of Huege et al. will read on the claimed specific

surface area recited in the instant claims.

The Examiner argues further that the previously mentioned Declaration of Professor Jean-Paul Pirard

is not sufficient to overcome this grounds of rejection, since the Declaration only shows the

difference between the specific surface area and BET specific surface area in a porous matter.

However, if the solid matter in Huege et al. is non-porous, or with negligible porosity, the specific

surface area of Huege et al. will continue to read on the claimed specific surface area recited in

Applicant's pending claims.

US 5,616,283 (Huege et al.) is assigned to a commonly owned entity of the Applicant in the present

application. As such, Applicant is well aware of the teachings of this reference. In the broadest sense,

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the reference describes a composition for a pumpable lime slurry adapted for use as a replacement

for caustic solutions. As such, the material being described in the Huege et al. reference relates to

a suspension of slaked lime particles. Note, for example, the Abstract of Huege et al.:

A composition for a pumpable lime slurry which is adapted for use as a replacement

for caustic solutions is formed by combining a dispersing agent in lime and water to

form an aqueous slurry.

Also note Col. 3, lines 51-53 of Huege et al.:

A fine particle size ensures longer <u>suspension of the particles</u> (Applicant's emphasis)

and results in a better reactivity of the lime slurry.

Applicant is including as Attachment One to this Response pages 172-177 and pages 194-201 of the

"Boynton Treatise": "Chemistry and Technology of Lime and Limestone." This particular treatise

is considered a fundamental text by those skilled in the limestone industry which is used as a

reference book and teaching tool by engineers, scientists and others in the relevant industry.

With reference to Table 6-2 on page 173 and also to page 195 of Attachment One, it can be seen that

quicklime has a degree of porosity which varies generally from a porosity of about 18 to 54 %.

It is well known that slaked lime is more porous than quicklime. Indeed upon extinction of quicklime

during the slaking process, the slaked lime which is obtained thereby undergoes expansion. As a

matter of consequence, with respect of quicklime from which it comes, slaked lime is more porous

and its density (also called specific gravity) decreases. It is known that slaked lime presents a

specific gravity about 1.5 times less than quicklime.

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As it can be seen in the Boynton treatise, the specific gravity (or density) of quicklime is about 3.34

(page 195), while the specific gravity of high calcium slaked lime is about 2.3 - 2.4 (see page 200).

Thus, the specific gravity is a value that is decreasing when porosity increases (see specific gravity

section – page 195).

The Examiner's attention is also directed to page 172 of the same treatise, which states in part that:

"The factors of porosity, density and pore size distribution are inter-related and exert

a profound influence on such standard measurable properties of quicklime as

reactivity, available lime, and the particle size distribution and surface area of the

resulting hydrated lime. A porous lime usually has low shrinkage; a dense lime of

low porosity has high lineal shrinkage."

This language clearly lends further support for the previously advanced assertions regarding the

specific gravity and porosity of quicklime and slaked lime. As a result, it should be clear that the

solid matter described in the Huege et al. reference is, in fact, porous and that the Examiner's

argument on this point has, respectfully been traversed.

Claims 1-6 are now thought to be allowable over the art of record and an early notification of the

same would be appreciated.

Respectfully submitted,

Date: Jan 20, 2010

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# Chemistry and Technology of Lime and Limestone

SECOND EDITION

ROBERT S. BOYNTON

Consultant

A Wiley-Interscience Publication

JOHN WILEY & SONS, INC.

New York • Chichester • Brisbane • Toronto

Serial No.: 10/56 Filed: 06/12

Attachment One 10/565,715 06/12/2006

## A NOTE TO THE READER

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behavior. The degree of lineal shrinkage increased proportionately with the total impurity contents of the dolomites; the greater the impurity content, the greater the shrinkage.

In the 1970s a Canadian, A. Job, confirmed many of the findings of Murray and Hedin in basic research on calcination using hot stage microscopy, dilatometry, porosimetry, and the scanning electron microscope.23 Invariably, he observed, from about 15 widely divergent limestone and dolomite species, that during preheating an average of 2% expansion occurred and that after calcination lime particles contracted in varying degrees. The most finely crystalline stone expanded the least and contracted the most after calcination, whereas the coarse crystalline types expanded the most and shrunk the least. A dolomitic stone exhibited a contrast. It expanded slowly until 615°C, then contracted slightly and briefly and a second expansion occurred until 960°C, when there was a second shrinkage. He conjectures that this quadruple volume change is due to double decomposition of the Mg and Ca carbonates. As a generalization, he concluded that dilation and contraction is controlled by crystal size, and of the variations in dissociation temperature of the stones, the calcination temperature is greater for a well-formed, highly crystallized stone than for a poorly crystalline type and is also greater for stone that is dense and possesses large crystals in contrast to porous, small crystalline stone. Hot stage microscopy revealed the formation of cracks in some large crystalline types during dilation. After calcination these cracks did not close, at least, not completely, during contraction. Such lime, being structurally weakened, would probably degrade in pneumatic handling systems. No such cracks were revealed in the fine-grained limestone specimens.

# Porosity and Density

The factors of porosity, density, and pore size distribution are interrelated and exert a profound influence on such standard measurable properties of quicklime as reactivity, available lime, and the particle size distribution and surface area of the resulting hydrated lime. A porous lime usually has low shrinkage; a dense lime of low porosity has high lineal shrinkage. When calcination temperatures are increased or constant temperatures in a medium to high calcination range are retained, there is diminution in porosity (the converse of Table 6-1 on shrinkage).

Data on porosity measurements obtained from 41 calcinations of calcite under diverse temperature-time combinations are contained in Table 6-2, based on Murray's research. In a series of tests in a muffle furnace on 10 high calcium limestones, Fischer beserved that retention time of 1 to 4 hr had little or no effect on porosity, surface area, or reactivity at mild calcina-

Table 6-2. Properties of quicklime as affected by temperature and time of calcination

| Calcina-       | of           | x. T<br>bed<br>(°C) | Reten-<br>tion<br>time<br>(min) | Time to<br>reach<br>1700°F<br>(min) | Activity coefficient $\Delta T_{\delta}$ | Bulk<br>specific<br>gravity | Poros-<br>ity<br>(%) | Volu-<br>metric<br>shrinkage<br>(%) |
|----------------|--------------|---------------------|---------------------------------|-------------------------------------|--|-----------------------------|----------------------|-------------------------------------|
| 19-1           | 1850         | 1010                | 474                             | 182                                 | 33,4                                     | 1.78                        | 46.6                 | 15.1                                |
| 19-2           | 1850         |                     | 230                             | 88                                  | 35.2                                     | 1.74                        | 47.8                 | 13.1                                |
| 19-3           | 1834         |                     | 185                             | 72                                  | 35.2                                     | 1.73                        | 48.1                 | 12.6                                |
| 19-4           | 1857         |                     | 103                             | 39                                  | 36.3                                     | 1.73                        | 48.1                 | 12.6                                |
| 19-5           | 1850         |                     | 97                              | 37                                  | 36.3                                     | 1.73                        | 48.1                 | 12.6                                |
| 19-6           | 1760         |                     | 82                              | 34                                  | 35.5                                     | 1.72                        | 48.4                 | 12.1                                |
| 19-7           | 1727         |                     | 74                              | 31                                  | 36.3                                     | 1.72                        | 48.4                 | 12.1                                |
| 19-8           | 1707         | 931                 | 67                              | 29                                  | 33.2                                     | 1.72                        | 48.4                 | 12.1                                |
| 21-1           | 2020         | 1104                | 474                             | 163                                 | 30.2                                     | 1.80                        | 46.0                 | 16.0                                |
| 21-2           | 2018         | ~                   | 230                             | 79                                  | 34.3                                     | 1.76                        | 47.2                 | 14.1                                |
| 21-3           | 2020         |                     | - 103                           | 35                                  | 33.6                                     | 1.78                        | 46.6                 | 15.1                                |
| 21-4           | 2023         |                     | 95                              | 3.3                                 | 30.5                                     | 1.87                        | 43.9                 | 19.1                                |
| 21-5           | 2023         |                     | 92                              | 32                                  | 30.9                                     | 1.86                        | 44.2                 | 18.7                                |
| 21-6           | 2020         |                     | 82                              | 28                                  | 26.0                                     | 1.89                        | 43.3                 | 20.0                                |
| 21-7           | 2000         |                     | 76                              | 27                                  | 26.6                                     | 1.87                        | 43,9                 | 19.1                                |
| 21-8           | 2000         |                     | 67                              | 23                                  | 22.3                                     | 1.92                        | 42.4                 | 21.3                                |
| 21-9           | 1853         |                     | 63                              | 24                                  | 11.4                                     | 2.10                        | 37.0                 | 28.0                                |
| 21-10          | 1780         |                     | 49                              | 20                                  | 14.2                                     | 1.96                        | 41.2                 | 22,9                                |
| 21-11          | 1765         | 963                 | 46                              | 19                                  | 12.0                                     | 2.05                        | 38.4                 | 26.2                                |
| 23-1           | 2218         | 1214                | 474                             | 146                                 | 31.5                                     | 1.81                        | 45.7                 | 16.5                                |
| 23-2           | 2220         |                     | 474                             | 146                                 | 33.2                                     | 1.79                        | 46.3                 | 15.5                                |
| 23:-3          | 2223         |                     | 308                             | 95                                  | 33,8                                     | 1.79                        | 46.3                 | 15.5                                |
| 23-4           | _            |                     | 230                             | 71                                  | 31.9                                     | 1.81                        | 45.7                 | 16.5                                |
| 23-5           | 2229         |                     | 127                             | 39                                  | 7.9                                      | 2.21                        | 33.7                 | 31.6                                |
| 23-6           | 2225         |                     | 103                             | 36                                  | 8.4                                      | 2.20                        | 34.0                 | 31.3                                |
| 23-7           | 2218         |                     | 82                              | 25                                  | 11.4                                     | 2.17                        | 34,9                 | 30.3                                |
| 23-8           | 2204         |                     | 67                              | 21                                  | 6.4                                      | 2.30                        | 31.0                 | 34.3                                |
| 23-9           |              |                     | 66                              | 20                                  | 6.7                                      | 2.34                        | 29.7                 | 35.4                                |
| 23-10<br>23-11 | 2158<br>2184 | 1195                | 48<br>47                        | 15<br>15                            | 5.1<br>5.5                               | 2.35<br>2.47                | 29.4<br>25.8         | 35.7<br>38.8                        |
|                |              |                     |                                 |                                     |  |                             |                      |                                     |
| 25-1           | 2362         | 1294                | 474                             | 136                                 | 20.8                                     | 1.88                        | 43.5                 | 19.6                                |
| 25-2<br>25-3   | 2397         |                     | 308                             | 86                                  | 30.2                                     | 1.83                        | 45.0                 | 17.4                                |
|                | 2400         |                     | 230                             | 65 ·                                | 28.7                                     | 1.85                        | 44.5                 | 18.3                                |
| 25-4<br>25-5   | 2396         |                     | 103<br>100                      | 29                                  | 7.2                                      | 2.40<br>2.21                | 27.9                 | 37.0                                |
| 25-5<br>25-6   | 2412         | 1322                | 95                              | 28                                  | 9.6<br>3.6                               |                             | 33.6                 | 31.6                                |
| 25-0<br>25-7   | 2412         | 1322                | 93<br>82                        | 26<br>23                            | 2,2                                      | 2.61<br>2.63                | 21.6<br>21.6         | 42.1<br>42.1                        |
| 25-7<br>25-8   | 2397         |                     | 82<br>74                        | 23<br>21                            |  |                             |                      |                                     |
|                |              |                     |                                 |                                     | 2.0                                      | 2.71                        | 18.6                 | 44.2                                |
| 25.9           | 2407         |                     | 67                              | 19                                  | 2.6                                      | 2.65                        | 20.4                 | 42.9                                |
| 25-10<br>25-11 | 2402<br>2341 | 1283                | 49<br>48                        | 14<br>14                            | 2.0                                      | 2.63                        | 21.0                 | 42.7                                |
| 23-11          | 2341         | 1200                | 40                              | .14                                 | 2,4                                      | 2.67                        | 19.8                 | 43.5                                |

tion temperatures of 1750-1950°C (954-1066°C). The bulk densities of these quicklimes remained constant. He also discovered that shock calcination (i.e., sudden application of high temperature without preheating) invariably densified the resulting oxide, usually abnormally, except at very low temperature (1780°F). Staley and Greenfeld<sup>22</sup> obtained somewhat similar results with a high calcium stone of 98.5% CaCO<sub>3</sub> content, as indicated in Figs. 6-5 and 6-6 on the effect of time and temperature on surface area.

Murray also studied porosity distribution with a specially designed porosimeter and concluded that the type of porosity that contributes the most to high surface area are the lowest average pore sizes, measured in angstrom units. He speculates that if two quicklimes have the same percentage of porosity, but one has pores with an average diameter of 1000 Å and the other 40 Å, the internal surface area of the lime with the larger pores is only 4% of the surface area of the smaller.

Generally Murray was able to obtain higher porosity, surface area, and reactivity in calcination experiments with Iceland Spar than with most

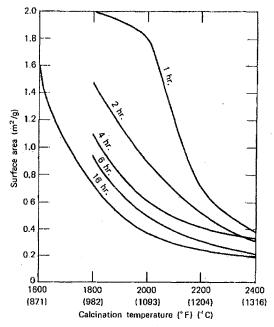


Fig. 6-5. Relation of surface area to calcination temperature.

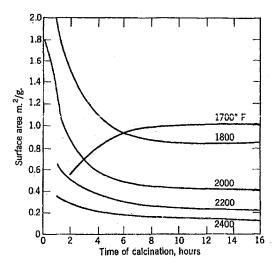


Fig. 6-6. Relation of surface area to duration of calcination

limestones, which indicates the adverse effect of impurities on reactivity and quality.

Hedin's explanation of increased density and shrinkage is that the CaO molecular crystals that form through dissociation are simultaneously uniting into progressively larger crystallites. <sup>14</sup> In tests with calcite through microphotography, he has calculated that these crystals at 900°C, the start of dissociation, are only about 0.1  $\mu$ ; at 1000°C they are 1  $\mu$ , owing to coalescence of these crystallites. At 1100°C a still larger coherent mass of crystallites is formed that becomes steadily more strongly bonded together with increasing temperature. Figure 6-7 illustrates this enlargement of crystals, and the accompanying explanation by Hedin elucidates the cause of shrinkage and densification. Fischer's<sup>21</sup> findings on the formation of crystallites coincided with Hedin's.

Mayer and Stowe, <sup>20</sup> adhere to this same crystallite theory and have observed through X-ray the inexorable buildup of the crystallites as calcination temperatures are raised. They estimate that the average CaO crystal is increased about a thousandfold (from 0.1  $\mu$  to 100  $\mu$ ) between initial calcination at minimum dissociation temperature and at sintering temperature of about 3000°F (1650°C), when the lime is completely dead-burned. However, with dolomite they observed that the accretion of the CaO crystallites is more rapid than its MgO component, resulting in much larger ultimate CaO crystals. Their explanation of this phenomenon is that the

CaO molecules possess lower "bond energy" than their MgO counterparts and, as a result, migrate more easily throughout the matrix. They also commented that there is no lineal change in the apparent density of the original stone fragment as these crystallites accrete, up to the dead-burned stage when the physical size of the particle shrinks perceptively. Before the dead-burned stage, the only change in the molecular geometrics of the lump is immeasurable—namely, the corresponding reduction in pore space and surface area. Mayer and Stowe's research was predicated on two chemical-grade limestones, high calcium and dolomitic types from northern Michigan.

The true specific gravity of CaO is 3.34-3.40, but this only occurs when theoretically pure quicklime has been extremely dead-burned, yielding optimum shrinkage, densification, and zero porosity—virtually impossible to obtain commercially. Murray<sup>16</sup> experimentally produced in the laboratory limes of 3.30 specific gravity, but generally values in the 2.5-3.0 range are considered very hard-burned, unreactive lime. Azbe<sup>12</sup> claims the ultimate in calcination should be highly porous, reactive lime of only 1.45-1.65 specific gravity, which would indicate a porosity of over 50%. Practically, such lime would be very difficult to manufacture with any consistency and economy.

A summary of Murray's on apparent specific gravity (bulk density) of 43 high calcium limestones reveals a range from 1.72 to 2.71; 25 of the 43 samples ranged between 1.72 and 1.96.

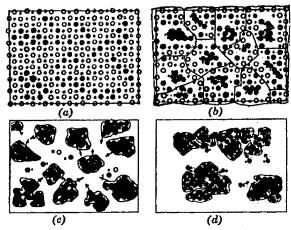


Fig. 6-7. Graphic display of how lime oxides gradually form much larger crystallites as calcination temperature increases. Gradual agglomeration of small crystals into steadily larger crystallites is illustrated sequentially in (a) through (d)

Murray observed that the general shrinkage pattern also occurs with pure calcite (Iceland spar). Figures 6-8 and 6-9 display the approximate 15% lineal reduction of a cube of calcite in a heating microscope at 500 and 1400°C.

### Effect of Stone Size

Since dissociation always penetrates gradually from the surface into the interior of the stone, the *larger* stone sizes are more difficult to calcine uniformly and require more time. Large cubical stone sizes of 6 in. (15.2 cm) and up are particularly difficult to calcine. To expel the CO<sub>2</sub> from such large stone, high temperatures are necessary to generate sufficient CO<sub>2</sub> pressure in the interior of the crystal lattice for the escape of the gas. Frequently these high temperatures (2300–2450°F range) overburn the surface layer of the stone, causing excessive shrinkage, which narrows and closes the pores and fissures. Pores are also clogged by the slagging effect of impurities (mainly SiO<sub>2</sub> and secondarily Al<sub>2</sub>O<sub>3</sub>) in the stone that are fluxed with lime, forming occlusions. Because of these stifled dissociation conditions, recarbonation of the surface and/or incomplete dissociation of the core (center of the stone) may occur, thus producing a dense, highly unreactive lime of low surface area, but one paradoxically underburned or uncalcined in the center.

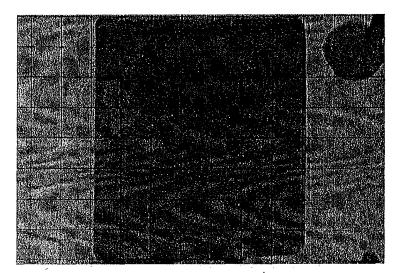


Fig. 6-8. Specimen of a calcite cube as seen in heating microscope at 500°C.

Milk-of-lime is a dilute lime hydrate in aqueous suspension and is the consistency of milk.

Pebble Lime is a physical shape of quicklime.

Quicklime is a lime oxide formed by calcining limestone so that carbon dioxide is liberated. It may be high calcium, magnesian, or dolomitic and of varying degrees of chemical purity.

Slaked lime is a hydrated form of lime, as a dry powder, putty, or aqueous suspension.

Soft-burned lime is a quicklime that is calcined at relatively low temperature. It is characterized by high porosity and chemical reactivity.

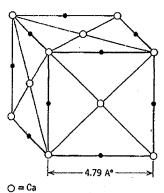
Type S hydrated lime (also called special hydrated lime) is an ASTM designation to distinguish a structural hydrate from a normal hydrated lime, designation Type N, that possesses specified plasticity and gradation requirements. It may be dolomitic or high calcium and is more precisely milled than Type N hydrates.

Unslaked lime is any form of quicklime.

Whitewash is synonymous with milk-of-lime, a dilute lime hydrate suspension.

### PHYSICAL PROPERTIES OF QUICKLIMES

COLOR. Generally quicklime is white of varying degrees of intensity, depending on its chemical purity. The purest types of quicklimes are the whitest. Less pure or improperly calcined types may have a slight ash gray, buff, or yellowish cast. The quicklime is invariably whiter than its derivative, limestone.



 $\bullet = 0$ 

Fig. 7-1. Crystal structure (unit cell) of calcium oxide.

ODOR. It possesses a faint but distinctive odor that is difficult to define. It is slightly "earthy" and pungent but not offensive.

TEXTURE. All quicklimes are crystalline, but the crystallite conglomerates vary greatly in size and spacing in their matrices. Some appear to be amorphous, but they are microcrystalline.

CRYSTAL STRUCTURE. X-ray diffraction reveals that a pure calcitic oxide crystallizes in the cubic system as depicted in Fig. 7-1. The edges of the cube are 4.797 Å in length, with calcium atoms located midway in between.

Magnesium oxide possesses the same cubic crystal lattice as CaO, except that the MgO crystal is slightly smaller and denser, with edge lengths of 4.203 Å. This accounts for the slightly higher average density of dolomitic quicklime.

The crystal lattice (AX type) is similar to the cubic arrangement for NaCl and is tabulated as follows:

|         | Coordination |                       | Sum of ionic       |        |
|---------|--------------|-----------------------|--------------------|--------|
| Crystal | number       | <i>a</i> <sub>0</sub> | radii <sup>a</sup> | Expt.  |
| CaO     | 6            | 4.797 Å               | 2.39 Å             | 2.40 Å |
| MgO     | 6            | 4.203 Å               | 2.05 Å             | 2 10 Å |

° Calculated ionic radii for coordination number 6 are as follows:  $Ca^{++} = 0.99 \text{ Å}$ ,  $Mg^{++} = 0.65$ , and  $O^{--} = 1.40$ .

POROSITY DENSITY. The degree of porosity of commercial quicklime varies widely in percent of pore space from 18 to 54%, with an average value of about 35%, depending on the structure of the limestone, temperature, and severity of calcination (see Table 6-2). Dead-burned dolomite has much lower porosity of 8-12%.

SPECIFIC GRAVITY. The *true* specific gravity of pure calcium oxide is 3.34, but this presupposes zero porosity, a condition that is impossible to achieve in manufacture. Values have been reported at 3.40, and lower, but 3.34 appears to be a generally recognized average value. Commercial limes may range as low as 3.0; pure dolomitic oxides may range as high as 3.5-3.6.

The apparent specific gravity varies similarly, from 1.6 to 2.8. Average values for commercial oxides are 2.0-2.2. Values for dolomitic quicklimes average about 3-4% more than the preceding. Dead-burned has the highest value of all—an average of 3.2.

BULK DENSITY. The same variance pertaining to specific gravity is prevalent as well as the added variable of the different physical size and gradation of the quicklime particle. The range in values in lb/ft³ is 48-70

(769-1121 kg/m³), with an estimated average of 55-60 lb/ft³ (881-961 kg/m³) for commercial quicklime of pebble size.² Lump size is about 10% lower, and ground or pulverized is 12-15% greater than this average value. (The larger the particle and the more restricted the gradation, the lower the bulk density.)

Values for dolomitic average 3-4% greater than those for high calcium.

HARDNESS. Hard-burned and sintered dolomitic quicklime lies between 3 and 4 on the Moh's scale. Ordinary quicklime is variable, but is usually between 3 and 2. The same broad divergence in hardness and strength in limestones is manifest in their derivative limes.

COEFFICIENT OF EXPANSION. The only values reported are  $145 \times 10^{-7}$  between 300 and 700°C and  $138 \times 10^{-7}$  between 0 and 1700°C<sup>3</sup>. These data probably only represent the magnitude of this measurement; certainly a variance would exist with commercial quicklimes.

ELECTRICAL RESISTIVITY. Resistivity of  $71 \times 10^8$  ohms/cm at 15°C (59°F), declining to 91 ohms at 1466°C (2671°F), has been calculated. The presence of nitrogen depresses values.

REFRACTIVE INDEX. The pure calcitic oxide is 1.83 and the value of commercial quicklime ranges betwen 1.70 and 1.82. A value of 1.736 for pure MgO means that dolomitic quicklime has a slightly lower value than CaO.<sup>4</sup> Both types possess slight refractive properties.

LUMINESCENCE. All lime oxides are very luminsecent at high temperatures in the calcining range of 900°C (1652°F) and higher; hence, origin of the term "limelight."

THERMAL CONDUCTIVITY. It has been estimated at 0.0015-0.002 cal/cm<sup>3</sup> sec °C temperature difference, but this value may be undependable.

HEAT OF FUSION. It is doubtful whether this has ever been accurately measured; 28,000 cal/mole has been estimated as the approximate value.

MELTING POINT. Recognized values for CaO are 2570°C (4658°F) and for MgO are 2800°C (5072°F), with dolomitic oxides intermediate.

A eutectic mixture of about 50% CaCO<sub>3</sub> and 50% CaO is reported to melt at 1240°C under high pressure of 30,000 mm.<sup>6</sup>

A recent investigation of the system CaO-MgO, involving X-ray diffraction and optical methods, that may comprise the most authoritative data, reveals a maximum solid solution of MgO in a CaO lattice of 17% weight and a maximum solid solution of CaO in the MgO lattice of 7.8% weight,

!

### **Definitions and Properties of Limes**

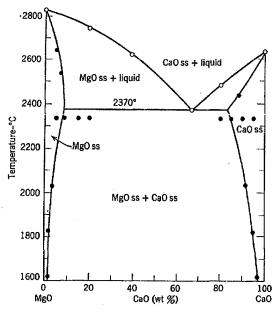


Fig. 7-2. Phase equilibrium diagram for system, CaO MgO. Solid circles are data points of solid solution, and open circles represent liquidus points.

both at temperatures of 2370°C. In both instances the extent of solid solution is higher than that reported by other investigators. Melting point for the eutectic 67% CaO and 33% MgO is 2370°C; for 100% CaO, 2625°C; for 100% MgO, 2825°C. Figure 7-2 shows the phase equilibrium diagram, calculated by these investigators.

HEAT OF COMBINATION. Same value as for heat of formation, given later.

BOILING POINT. Values for CaO are 2850°C (5162°F) and for MgO are 3600°C (6512°F), with dolomitic oxides intermediate.8

SPECIFIC HEAT. Figure 7-3 graphically reveals the range of mean values for high calcium and dolomitic quicklimes and MgO at temperatures from 0 to 2500°C. They encompass:

For high calcium from 0.17 to 0.32
For dolomitic from 0.185 to 0.319
For MgO from 0.195 to 0.316

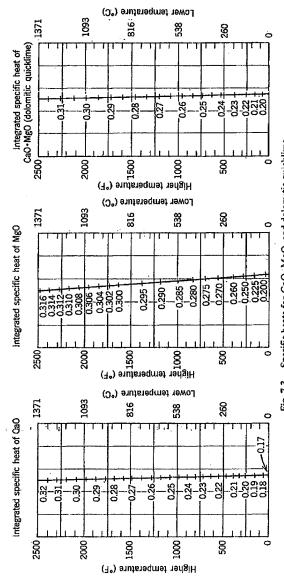


Fig. 7-3. Specific heats for CaO, MgO, and dolomitic quicklime.

These values increase gradually as the temperatures rise. Earlier investigators developed slightly different values than those just given 0.182-0.232 for CaO and 0.197-0.243 for CaO MgO (dolomitic).<sup>10,11</sup> The former values are preferred.

HEAT OF FORMATION. The value 151,900 cal/mole is generally recognized for CaO; for MgO (periclase) 143,750 cal/mole is the value at 298°C, but this latter value rises gradually to 174,050 cal/mole at 2000°C.<sup>12</sup>

ANGLE OF REPOSE. There is some variance in values with different quicklimes and with different particle sizes and gradations, but 50-55° for pebble sizes is a reasonable average for this measurement.

SOLUBILITY. See values of hydrated limes in the following section, since quicklime is converted to a hydrate before dissolution occurs.

HEAT OF SOLUTION. Heat of solution for CaO has been measured between 844.72 and 847.08 cal/g. <sup>13</sup> Solubility of MgO is so slight that this value may not be measurable.

SURFACE ENERGY. Surface energy of CaO at 23°C has been measured at  $1310 \pm 200 \text{ erg/cm}^2$ .

A value that is 330 erg/cm<sup>2</sup> higher than the corresponding CaO value has been calculated for MgO. Brunauer<sup>13</sup> estimates this value at a minimum of 1400 erg/cm<sup>2</sup>, about 300 units higher than the 1000-1040 erg/cm<sup>2</sup> for MgO calculated between 0 and 298° K by another source. The higher value is preferred.

#### PHYSICAL PROPERTIES OF HYDRATED LIMES

COLOR. All dry hydrates, except those that are quite impure, are extremely chalky in color, invariably whiter than their derivative quicklime. Overburning of quicklime may yield a faint yellowish cast in the resulting hydrate. Dark flecks of coarse particles are simply impurities, usually silica.

Individual pure hydroxide crystals are clean and colorless.

ODOR. Same approximate aroma as for quicklime.

FORM. It occurs as a fine powder. Fineness varies, but particles may be microcrystalline or colloidal size (submicron). For this reason, many people erroneously regard some forms of hydrate as amorphous. But X-ray reveals a definite crystal structural pattern for even the finest hydrates. <sup>15</sup> Coarse hydrate particles are clearly crystalline in appearance.

CRYSTAL STRUCTURE. The crystal is a hexagonal-shaped plate or prism with perfect basal cleavage, but the physical particle is of varying size since the microscopic crystallites agglomerate in varying degrees. Hedin describes the crystals in solid state as forming a "ditrigonal scalenohedral belonging to the hexagonal-rhombohedral system."

The crystal lattice (AX<sub>2</sub> type) of the unit cells is similar to the molecular arrangment for CdI<sub>2</sub>, depicted as follows and in Figs. 7-4 and 7-5 for both Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub>:

|                     |   | ination<br>nber | Edge length |          | Acute<br>angle |
|---------------------|---|-----------------|-------------|----------|----------------|
| Crystal             | Α | х               | of base     | Height   | of base        |
| Ca(OH) <sub>2</sub> | 6 | 3               | 3.5844 Å    | 4.8962 Å | 60°            |
| $Mg(OH)_2$          | 6 | 3               | 3.11 Å      | 4.74 Å   | 60°            |

SPECIFIC GRAVITY. The ranges in specific gravities for different commercial hydrates are as follows:

| High calcium              | 2.3-2.4 |  |
|---------------------------|---------|--|
| Highly hydrated dolomitic | 2.4-2.6 |  |
| Normal hydrated dolomitic | 2.7-2.9 |  |

The latter contains 25-35% MgO on an average. (Hedin calculated a value of 2.244 g/cm<sup>3</sup> for pure reprecipitated Ca(OH)<sub>2</sub> from X-ray diffraction data.)

APPARENT DENSITY. Values of 0.4-0.55 g/ml have been reported.

BULK DENSITY. As determined by the Scott method, a range in bulk density would be 25-40 lb/ft<sup>3</sup> (400-641 kg/m<sup>3</sup>) for commercial hydrates,

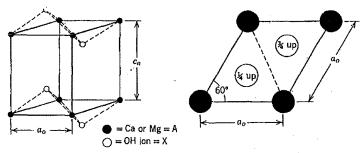


Fig. 7-4. Crystal structure (unit cell) of calcium hydroxide.

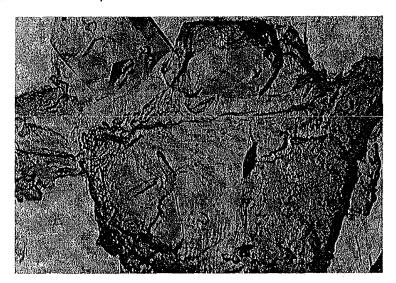


Fig. 7-5. Microphotograph clearly showing the single large crystals of  $Ca(OH)_2$  and its characteristic rhombohedron shape ( $50,000\times$ ).

with about 35 lb/ft<sup>2</sup> (561 kg/m<sup>3</sup>) an average value.<sup>2</sup> Degree of air entrainment affects bulk density values.

ANGLE OF REPOSE. There is a very wide range in angle degrees for different commercial hydrates, depending on particle size, moisture content, degree of aeration, and particularly the extent of the electrostatic charge. It may range from 15 to 80°, but 70° is considered most common by some authorities.

HARDNESS. It is intermediate between 2 and 3 on the Moh's scale, with 2.5 an average value reported for pure Ca(OH)<sub>2</sub> crystals.

REFRACTIVE INDEX. Values for both Ca(OH)<sub>2</sub> and MG(OH)<sub>2</sub> are similar, being 1.574 and 1.545 for the former and 1.559 and 1.580 for the latter. Crystals are uniaxially negative. Maximum index of double refraction is 0.029.

COEFFICIENT OF EXPANSION. It is  $3.34 \times 10^{-6}$  along the principal axis and  $0.98 \times 10^{-6}$  normal to it. Data is scant and of only academic interest.

SPECIFIC HEAT. The values would depend on the specific heats of the two reactants, CaO and MgO, discussed earlier, and water that forms the